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I could have wished to give equations expressive of the entire decompositions which take place, and it would be easy to do so were I to disregard, or consider as merely accidental, the substances formed at the same time. When the brominized oil is distilled, before or after treatment with alcoholic potash, nearly fifty per cent. of loss is incurred. The retort contains a black carbonaceous mass, occupying two-thirds of its capacity. A similar phenomenon occurs in the treatment with sodium; and at the same time, as already observed, a certain portion of caoutchin or turpentine, as the case may be, is regenerated.

The yellow oil of high boiling-point previously alluded to exists in very small quantity among the products formed by the action of sodium on brominized caoutchin; probably not more than one-tenth of the distillate boils above 200° C., whereas the yellow oil boils only a little below 300° C. The quantity in my possession was far too small to allow of a determination of this point. In composition, however, it agreed with that of cymole.

The crystalline substance was in exceedingly minute quantity. It is far from impossible that it may be the radical thymyl formed from its hydruret cymole by the action of the bromine. As it would have the composition $C_{40}H_{26}=2C_{20}H_{13}$, the probability is that it would be a crystalline solid.

The exceedingly high boiling-point of the yellow oil is such strong evidence of its being a polymeric condition of cymole, that I have provisionally named it *paracymole*.

Conversion of the Cymole from Turpentine and Caoutchin into Insolinic Acid.

Although the experiments detailed left little doubt of the identity of the cymole from turpentine and caoutchin with that from cumin oil, still the number of isomeric bodies continually being discovered is so great, that it was highly desirable to make a crucial experiment. The exceedingly characteristic properties of isolinic acid rendered it peculiarly suitable in the present instance. Dr. Hofmann has shown it to be a product of the oxidation of cuminic acid and cymole under the influence of chromic acid. The quantity of cymole in my possession was so small (about two drachms), that there would have been little hope of success had the reaction been less definite. On cohobating it with 8 parts of sulphuric acid, 8 pts. of bi-

chromate of potash, and 12 pts. of water, for a few minutes, white flocks became apparent; they continually increased until their bulk equalled that of the cymole employed. The crude acid was dissolved in ammonia, and, after filtration, precipitated by hydrochloric acid. It was washed, first with warm water, then with boiling alcohol, and finally with ether. Thus purified it was quite colourless. It was then dissolved in ammonia, and the solution evaporated until crystals of the acid salt began to form. The solution, rendered faintly alkaline by the cautious addition of ammonia, was precipitated by nitrate of silver, care being taken to keep it slightly alkaline, to prevent the separation of any insolinic acid. The salt, after drying at 100° until it ceased to lose weight, was ignited, during which operation it evolved the peculiar aromatic odour so characteristic of all the insolinates when heated strongly. In this manner I prepared three specimens, one from turpentine, another from caoutchouc, and a third from gutta percha. All three gave, by analysis, results corresponding sufficiently with the formula

$$C_{18}(H_6Ag_2)O_8.$$

Action of Sulphuric Acid on Caoutchin.

On slowly adding caoutchin to sulphuric acid (sp. gr. 1·845) in great excess, the latter becomes warm, and the greater part of the hydrocarbon dissolves, traces of sulphurous acid being at the same time evolved. On the addition of water, the greater part of the caoutchin rises in an altered state to the surface; it is in the form of a thick adhesive fluid of the consistence of molasses. On saturating the acid solution with chalk, a very small quantity of the lime-salt of a conjugate sulphuric acid was obtained. It is excessively soluble in water, and deposits small granular crystals from a concentrated solution. Dried at 200° C. it gave, by analysis, results agreeing with the formula $C_{20}H_{15}CaS_2O_6$.

On the Composition of Caoutchouc.

The only analyses of caoutchouc which I have seen are those of Faraday and the late Dr. Ure. That of the latter chemist is obviously incorrect, as he obtained 90 per cent. of carbon and only 9.1 of hydrogen, a result incompatible with the phenomena which take place under the influence of heat.

Faraday's analysis, made in the year 1826, probably exhibits almost exactly the true composition of pure caoutchouc. It gave carbon 87·2 and hydrogen 12·8 per cent. These numbers would require to be slightly modified, in consequence of the atomic weight of carbon, as now received, having a somewhat different value to that which was admitted at the time of the analysis. I analysed two small specimens (probably less pure than that examined by Faraday), which had formed in phials of the juice, with the annexed results. They were dried at 100°. The first specimen was dark brown, the second pale straw-coloured and almost transparent.

The first gave 86·1 p. c. C, 12·3 H, 0·9 ash, and 0·7 nitrogen, oxygen, and loss; the second 87·2 C, and 12·8 H.

I am anxious to call attention to the fact that the atomic constitution of caoutchouc appears to bear some simple relation to the hydrocarbons resulting from its decomposition by heat. The composition of caoutchouc coincides with that of isoprene and caoutchin, as found by analysis, to a degree which is remarkable, when we consider that caoutchouc, in addition to being non-crystalline, is scarcely capable of purification by chemical means. Additional evidence may be found in the smallness of the residue which is left on submitting caoutchouc to heat. The following results of the analyses will show the amount of confidence which may be placed in this idea:—

	Isoprene.	Caoutchin.	Caoutchouc.		
	Mean.	Mean.	Faraday.	C. G. W.*	
Carbon . .	88·0	88·1	87·2	86·9	87·3
Hydrogen .	12·1	12·0	12·8	12·4	12·1

The following table contains a summary of the physical properties of isoprene and caoutchin.

Table of the Physical Properties of Isoprene and Caoutchin.

Name.	Formula.	Boiling-point.	Specific gravity.	Vapour-density.	
				Experiment.	Calculation.
Isoprene .	$C_{10}H_8$	37° C.	0·6823 at 20° C.	2·44	2·349
Caoutchin .	$C_{20}H_{16}$	171	0·8420	4·65	4·699

* Ash deducted.

It will be seen from what has been said upon the composition of the above bodies, that they may equally be obtained from caoutchouc or gutta percha. When the latter substance is submitted to careful distillation, the phenomena are essentially the same as with the former. The distillate contains a small quantity of water, which, instead of being alkaline, as with caoutchouc, is powerfully acid. The acid is volatile, and appears to belong to one of the lower members of the series $C_nH_nO_4$. On neutralizing the acid liquid with potash or soda, the odour of a volatile base becomes very perceptible.

The oily distillate, as with caoutchouc, consists principally of the thick uninviting fluid called by Bouchardat, *hévéène*. I have not as yet minutely examined it, but believe it to bear a polymeric relation to caoutchin.

The amount of isoprene in the crude distillate is very small, probably not more than five per cent., and, as will readily be supposed with so volatile a fluid, much is lost in the subsequent purification. It is this circumstance which has prevented me from examining it so closely as could be desired.

The caoutchin constitutes about twenty per cent. of the distillate; it was sensibly less pure than that procured from caoutchouc, and more rectifications over sodium were necessary before it was obtained in a sufficiently pure state for analysis. This partly arises from the tenacious manner in which the volatile acids above alluded to adhere to it, and render treatment with alkalies essential previous to rectification. It is also accompanied by what we are too much accustomed to vaguely term empyreumatic products. These are of a readily oxidizable nature, and may be got rid of by rectification two or three times over hydrate of potash.

The following is a brief summary of the results of the above investigation:—

1. The isolation of isoprene, $C_{10}H_8$, the existence of which among the products of the destructive distillation of caoutchouc had not been proved.

2. The production of an apparently definite oxide of the hydrocarbon $C_{10}H_8$, by the agency of ozone spontaneously generated.

3. The determination of the polymeric relation between isoprene and caoutchin.

4. The conversion of turpentine and caoutchin into the hydruret of thymyl or cymole.

5. The production of paracymole.

6. The determination of the products of the destructive distillation of gutta percha.

XXIV.—*On the Double Sulphides of Copper and Iron.*

By Frederick Field, F.R.S.E.

About two years ago, I made a verbal communication to the Chemical Society, upon certain double sulphides of copper and iron, produced by the fusion of the native compounds of those metals containing sulphur and oxygen. The experiments which were then enumerated, and which had extended at intervals over several years, have lately been resumed, and now, in a more complete form than heretofore, may perhaps be not deemed wholly uninteresting.

In countries where coal and labour are expensive, and building materials for furnaces, such as fire-bricks, fire-clay, &c., have to be economized as much as possible, it becomes necessary to devise some means in the smelting of copper ores, whereby fuel may be saved, and damage of the furnace alleviated. The process of roasting poor regulus, into a sulphide richer in copper, is that usually resorted to in England, but this roasting acts at the same time, very severely upon the sides of the furnace, as the slag, consisting to a great extent of oxide of iron, combines with the silica of the clay and of the bricks, forming silicate of iron. To avoid this difficulty, advantage is taken of the fact, that oxide and sulphide of copper mutually react upon each other, forming sulphurous acid and metallic copper—

$$2\,CuO + Cu_2S = 4\,Cu + SO_2$$

so that when an excess of the latter is employed, combined at the same time with more or less sulphide of iron, a rich regulus is produced, and the process of roasting is obviated. For example, if into a mass of fused regulus of low percentage, a few hundred weight of the carbonates of copper are introduced, and the whole brought to a state of fusion, the oxide of iron formed combines with the silica of the ore, producing a fusible slag, and a great por-

tion of the sulphur is oxidized at the expense of the oxygen contained in the carbonates. By adopting this method, regulus of a very high percentage may be obtained, and even metallic copper, if sufficient oxygen be present in the mineral to convert the whole of the sulphur into sulphurous acid. Practically speaking, however, this latter plan is seldom or never adopted, the smelter preferring to tap the regulus when it contains from 40 to 50 per cent. of copper, as if richer, the slags invariably contain much of that metal.

Many analyses have been made of the double sulphides of copper and iron, technically known as regulus, but probably owing to the ores themselves containing many other metals, such as tin, arsenic, antimony, and occasionally silver, it can scarcely be wondered at that the results of the investigations of various chemists upon this particular subject are not very concordant. From my own experience I am led to believe, that copper regulus always has a certain definite composition, and analyses of many specimens, collected from different quarters of the world, fully confirm the idea.

It appears that the copper invariably exists in the state of disulphide (Cu_2S) in regulus, associated with iron in various states of sulphuration. The sulphides of iron seem to exist in certain relative proportions, and the richness or poverty of the regulus in copper, to depend upon the number of the equivalents of disulphide in combination with them. It cannot be denied that certain facts seem to militate against this view, as for example, the action of hydrochloric acid upon the compound. Regulus of from 25 to 50 % copper, generally evolves sulphuretted hydrogen copiously, when treated with this acid, whilst that containing from 60 to 80 % is scarcely acted upon at all; but, nevertheless, the proportions of copper, sulphur, and iron, are so invariable, as to lead us to suppose that it is the great excess of disulphide of copper, which shields or protects the sulphides of iron from the acid, rather than that those sulphides have changed their chemical condition. And this case is not without a parallel. Silver, so readily oxidized by nitric acid, is not affected by that re-agent when alloyed with an excess of gold; neither, by means of hydrochloric acid can zinc be separated from copper, when the latter is in great excess; and in like manner when the number of atoms of disulphide of copper, combined with the iron-compound are diminished, much of the iron is dissolved, which, under other circumstances, would remain unaffected. It is, therefore, evident that no results can be

deduced as to the state in which the iron exists, by measuring the quantity of sulphuretted hydrogen evolved by the action of hydrochloric or sulphuric acid.

When regulus is repeatedly roasted, and the slag which accumulates upon the surface is skimmed off, a point is arrived at, when all the iron is withdrawn, and a pure disulphide of copper remains, having exactly the same specific gravity, physical appearance, and chemical composition, as the native disulphide, copper-glance. The sulphides of iron are all decomposed before the sulphide of copper is attacked, and it would almost appear that this compound plays the part of a base, as regards the sulphides of iron, and that the more concentrated the regulus becomes, the more basic is its composition. If a small quantity of oxide or carbonate of copper be dropped into a fused mass of the sulphide of iron, a disulphide of copper is produced, exercising a certain influence upon the whole compound with regard to the solvent action of acids.

Regulus appears to me to consist of one atom of sesquisulphide of iron Fe_2S_3, one atom of protosulphide FeS, and two atoms of disulphide Fe_2S, associated with disulphide of copper. Thus, a portion of clean regulus from a furnace yielded on analysis—

Copper	36·12
Iron	36·78
Sulphur	27·08
	99·98

or $(3\,Cu_2S)\ Fe_2S_3$, FeS, $2\,Fe_2S$. On roasting this compound for some hours, the regulus yielded—

Copper	49·71
Iron	25·34
Sulphur	24·85
	99·90

or $(6\,Cu_2S)\ Fe_2S_3$, FeS, $2\,Fe_2S$.

Again, after further roasting and skimming, another sample was subjected to analysis, and the results were as follows:—

Copper	61·34
Iron	15·61
Sulphur	22·90
	99·85

or $(12\,Cu_2S)\ Fe_2S_3$, FeS, $2\,Fe_2S_3$.

Although the native yellow copper pyrites has a different composition, the blue sulphides seem to follow the same law, as the artificially prepared regulus. Thus a very pure specimen yielded me—

Copper	54·21
Iron..	21·43
Sulphur	24·12
	99·76

or $(8\,Cu_2S)\,Fe_2S_3, FeS, 2\,Fe_2S,$

which requires—

Copper	54·93
Iron	21·04
Sulphur	24·03
	100·00

It is interesting to observe the rapid decrease in the proportion of iron, in comparison with the sulphur, as the copper augments. When the regulus contains 36 % of the latter metal, it contains also 36 % iron, and about 27 % sulphur. At 50 % of copper, the sulphur and iron are in nearly equal proportions. At 60 % the iron is reduced to 16·5 %; and the sulphur to 23 %, while at 80 % copper, all the iron has disappeared, and 20 per cent. of sulphur remains.

In the appended table, a tabular form of the theoretical construction of regulus is given, as well as the results of some experiments. It will be observed on examination, that the practical results agree very closely with the theoretical numbers, from which it certainly seems probable, to say the least, that these compounds have a definite constitution, and are not accidental admixtures, as is generally maintained.

Composition of the Double Sulphides of Copper and Iron.

	Calculated.			Experiment.				
	Copper.	Iron.	Sulphur.	Copper.	Iron.	Sulphur.		
(Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	17·20	52·68	30·10	....	....	....	..	..
(2 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	28·09	43·36	28·32	....	....	....	..	..
(3 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	36·09	36·84	27·06	36·12	36·78	27·08	..	..
(4 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	41·83	32·02	26·14	....	....	....	..	..
(5 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	46·24	28·32	25·43	46·34	28·19	25·27	..	..
(6 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	49·74	25·38	24·86	49·71	25·34	24·85	..	..
(7 Cu_2S) Fe_2S_3, FeS, 1 Fe_2S	52·57	23·00	24·41	52·48	22·89	24·32	..	..
(8 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	54·93	21·02	24·03	54·21	21·13	24·12	Native blue Sulphide.	
(9 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	56·91	19·36	23·71	....	....	....	..	..
(10 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	58·60	17·94	23·44	....	....	....	..	..
(11 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	60·07	16·72	23 20	....	....	....	..	..
(12 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	61·34	15·65	23·00	61·34	15·61	22·90	..	..
(13 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	62·46	14·71	22·82	....	....	....	..	..
(14 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	63·45	13·88	22·65	....	....	....	..	..
(15 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	64·34	13·13	22·52	....	....	....	..	..
(16 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	65·14	12·46	22·38	....	....	....	..	..
(17 Cu_2S) Fe_2S_3, FeS, 2 Fe_2S	65·84	11·86	22 27	....	....	....	..	..

XXV.—*On the Hydrocarbons produced by Destructive Distillation of Boghead Coal.*

By C. Greville Williams.

It is well known that when Frankland's and Kolbe's admirable researches on the organic radicals were first published, the formulæ adopted assumed those bodies to possess a condensation to two volumes.* M.M. Laurent and Gerhardt, in accordance with their system, considered themselves justified in doubling Frankland's formulæ, thus making the condensation of the radicals the same as that of the hydrocarbons generally, viz., to four volumes. But this appearing to remove from methyl and ethyl the characters of radicals in the electro-chemical sense of the term, they preferred to regard them as homologues of marsh-gas.

The progress of science showed, however, that although Laurent and Gerhardt were justified in doubling the formulæ, it was going too far to refuse the bodies in question the position of radicals: for Brodie and others have conclusively proved the derivation of these bodies from a double molecule of hydrogen. It was reserved for M. Wurtz to show that each molecule might be replaced by a different group, and thus to place the vapour-volume of the radicals altogether beyond dispute.†

The marsh-gas family, closely allied to the radicals in character, and belonging to the same type, are peculiarly liable to be confounded with them. The difficulty is moreover increased from the fact, that each alternate homologue of marsh-gas is isomeric with one of the radicals. This will become plain on inspection of the following table:—

Marsh-gas series.			Methyl (*radical*) series.	
Hydride of	Methyl	C_2H_4		
„	Ethyl	C_4H_6	Methyl	C_4H_6
„	Propyl	C_6H_8		
„	Butyl	C_8H_{10}	Ethyl	C_8H_{10}
„	Amyl	$C_{10}H_{12}$		

* In order to preserve uniformity between this and the previous papers on the same subject, I use the old notation, O = 8 and 2 HO = 4 vols.

† Ann. Ch. Phys. [3], xliv, 275.

Marsh-gas series.			Methyl (*radical*) series.	
Hydride of	Caproyl	$C_{12}H_{14}$ . . .	Propyl	$C_{12}H_{14}$
„	Œnanthyl	$C_{14}H_{16}$ . . .		
„	Capryl	$C_{16}H_{18}$ . . .	Butyl	$C_{16}H_{18}$
„	Pelargonyl	$C_{18}H_{20}$ . . .		
„	Rutyl	$C_{20}H_{22}$ . . .	Amyl	$C_{20}H_{22}$
„	Euodyl	$C_{22}H_{24}$ . . .		
„	Lauryl	$C_{24}H_{26}$ . . .	Caproyl	$C_{24}H_{26}$

While endeavouring to get a clue to the true nature of the indifferent hydrocarbons from Boghead naphtha, I was naturally led to pay particular attention to Dr. Hofmann's experiments on the action of heat upon valerianic acid. They were considered to prove the hydrides of the radicals high up in the series to be unable to endure a red heat: for he says,—"It appears that this term (C_8H_{10}) unable to exist at the prevailing temperature, is broken up into the more stable compounds of the series, C_nH_n, the excess of hydrogen being eliminated either in the form of marsh-gas, or as water formed by the reduction of carbonic acid to carbonic oxide;" and again,—"The members of this series appear to be far less stable than the hydrocarbons containing an equal number of carbon and hydrogen-equivalents." Further, "The instability of these substances would also explain why we have not hitherto obtained a member of the marsh-gas series, derived from the fatty acids in the various tars and naphthas which have been examined."*

It is curious to observe that while Dr. Hofmann, at the time of writing the paper alluded to, regarded bodies of the marsh-gas class, as high up even as C_8H_{10}, as unable to exist at a red heat, Frankland† had previously stated his belief that hydride of amyl would be found to exist among the products of the destructive distillation of wood and coal at carefully regulated temperatures. The paragraph is as follows;—"It is not impossible, that by regulating the temperature at which the destructive distillation of wood and coal is carried on, considerable quantities of hydruret of amyl might be cheaply obtained, which, as illuminating material, would surpass almost every other in convenience and brilliancy."

In my investigation "On some of the Products of the Destructive Distillation of Boghead Coal."‡ I showed the naphtha pro-

* Chem. Soc. Qu. J., iii, 123. † Ibid, p. 43.
‡ Philosophical Transactions, 1857.

duced by distilling boghead coal at low temperature to be a mixture of three classes of hydrocarbons, viz., homologues of benzole, of olefiant gas, and a series having the ultimate composition, boiling points, and density, both in the fluid and gaseous states, of the radicals of the alcohols. I stated, however, that they might also be regarded as the isomeric hydrides. The inertness of the bodies in question, and the absence of all reactions, allowed no crucial experiment to be made; nevertheless their physical properties so exactly corresponded with the radicals, that it was difficult to regard them as being merely isomers. This will appear evident on reference to the annexed table, extracted from my first paper on Boghead Naphtha :—

Comparative Table of the Physical Properties of the Radicals with the Hydrocarbons from Boghead Naphtha.

Radicals.	Boiling-Points.					Densities.				Vapour-Densities.				
	Frankland.	Kolbe.	Wurtz.	Brazier and Gossleth.	C. G. Williams.	Frankland, at 11°.	Kolbe, at 18°.	Wurtz, at 0°.	C. G. Williams, at 18°.	Frankland.	Kolbe.	Wurtz.	G. C. Williams.	Theory.
					Mean.									
Propyl $C^{12}H^{14}$	...	...	...	...	68°	...	...	...	0·6745	...	...	...	2 96	2·97
Butyl $C^{16}H^{18}$	...	108°	106°	...	119°	...	0·6940	0·7057	0·6945	...	4·053	4·07	3·88	3·94
Amyl $C^{20}H^{22}$	155°	...	158°	...	159°	0 7704	...	0·7413	0·7365	4·899	...	4 956	4·93	4·91
Caproyl $C^{24}H^{26}$	...	...	202°	202°	202°	...	...	0·7574	0·7568	...	...	5·983	5·83	5·87

It will be observed that the only discrepancy of any moment is in the case of butyl, or hydride of capryl, the boiling point of which is 12° C. too high. This fact (which I was at first inclined to attribute to insufficient purification) induced me to spare no pains in determining the boiling point of the substance alluded to. The plan adopted being fully described in the original paper, need not be detailed here. It is necessary to state, however, that no amount of purification was found capable of reducing the boiling point below 119° centigrade.

Dürre, of Magdeburg,* repeated my experiments with great care on a naphtha of similar properties to that examined by me, but derived from brown coal, and the boiling point of the hydrocarbon of the formula $C_{16}H_{18}$ differed by only half a degree centigrade from that found by me.

* Edinburgh New Philosophical Journal, October 1859.

The above experiments were, however, quite insufficient to determine so delicate a point as that in view, in the absence of all decisive reactions, and it seemed almost impossible for merely isomeric bodies to possess properties so nearly identical. Moreover, it is quite plain, that as bodies so closely allied to the alcoholic radicals as the olefiants and the hydrides of the positive radicals, are formed during destructive distillation, there is no obvious reason why the radicals themselves, formed as they are on the same type, and being products of the decomposition of the hydriodic ethers, should not be produced under the same circumstances.

It struck me, however, that some light might be thrown upon the question by ascertaining whether the tar from Boghead coal contained a hydrocarbon unacted upon by acids, and distilling at a lower temperature than the substance provisionally termed propyl; it being evident, that as ethyl is a gas, a mixture of the true radicals should not contain a fluid boiling below propyl.

I have succeeded in obtaining a little Boghead naphtha of sufficient volatility to enable me to try this experiment. After purification by the method described in my previous paper, a liquid was obtained boiling between 30° and 40° centigrade.

0·1636 gramme gave 0·4990 carbonic acid, and 0·2460 water—

Experiment.		Calculation.		
Carbon . .	83·2	C^{10}	60	83·3
Hydrogen . .	16·7	H^{12}	12	16·7
			72	100·0

The vapour-density determined by Gay Lussac's method, gave the annexed result:—

Atmospheric pressure . . .	762 m.m.
Pressing column of oil reduced to millimetres of mercury . .	22·3
Difference of level	60·0
Temperature of vapour . . .	102° cent.
Volume of Vapour	48·0 c.c
Weight of substance . . .	0·1110 gramme.

The formula $C_{10}H_{12}$ = 4 volumes requires:—

10 volumes carbon-vapour .	0·8290·10 = 8·2900
24 volumes hydrogen . .	0·0692·24 = 1·6608
	9·9508
	$\frac{9·9508}{4}$ = 2·48395

Experiment.	Theory $C_{10}H_{12}$ = 4 vols.
2·575	2·484

It is evident from the above numbers, that the most volatile portion of Boghead naphtha contains a considerable quantity of hydride of amyl, and in all probability, therefore, the indifferent hydrocarbons are homologues of marsh-gas, and only isomeric with the true alcohol-radicals. It is evident that the formula of hydride of amyl corresponds to certain compound radicals; this is a question upon which we are not, at present, in a position to speculate.

I have found that the hydriodic ethers, and consequently the true radicals and their innumerable derivatives, may be produced from the above hydrides by a tolerably simple series of operations. On passing through a red-hot tube, the liquid hydrides are converted into olefiants of lower formula, with evolution of several gaseous products. The olefiants, by cohobation with fuming hydriodic acid, yield the hydriodic ethers thus:—

$$\underbrace{C_nH_n + HI}_{\text{Olefiant.}} = \underbrace{C_nH_{n+1}, I}_{\text{Hydriodic ether.}}$$

The process, although theoretically and practically simple enough, involves such a loss of material, that it will probably be some time before the investigation I am making upon it will be concluded. I had some hopes that the radicals and the hydrides would behave differently under the influence of heat, so as to enable me to distinguish between them by this means. The experiments as yet made in this direction appear to indicate, that, as in every other case known at present, they break up into nearly, if not absolutely, the same products.

XXVI.—*On the Synthesis of Succinic and Pyrotartaric Acids.*

By Maxwell Simpson, M.B.,

[Abstracted from the Philosophical Transactions, 1860, p. 61.]

Succinic acid bears the same relation to the diatomic alcohol glycol, that propionic acid bears to ordinary alcohol. Propionic acid can be obtained by treating the cyanide of the alcohol-radical with potash. Can succinic acid be obtained by treating the cyanide of the glycol-radical with the same reagent? or is it an isomeric acid that is formed under those circumstances?

$$\underbrace{C_4H_5Cy}_{\text{Cyanide of Ethyle.}} + O_2\left\{\begin{matrix}K\\H\end{matrix}\right. + 2HO = \underbrace{O_2\left\{\begin{matrix}C_6H_5O_2\\K\end{matrix}\right.}_{\text{Propionate of Potash.}} + NH_3$$

$$\underbrace{C_4H_4Cy_2}_{\text{Cyanide of Ethylene.}} + 2\left\{O_2\left\{\begin{matrix}K\\H\end{matrix}\right. + 4HO = \underbrace{O_4\left\{\begin{matrix}C_8H_4O_4\\K_2\end{matrix}\right.}_{\text{Succinate of Potash?}} + 2NH_3$$

The following experiments were performed with the view of determining this point.

Preparation of Cyanide of Ethylene.

This body was obtained by submitting bromide of ethylene to the action of cyanide of potassium. A mixture of two equivalents of the cyanide and one of the bromide, together with a considerable quantity of alcohol, was exposed in well-corked soda-water bottles to the temperature of a water-bath for about sixteen hours. To prevent the caking of the salt, it is advisable to have some coarsely powdered glass in the bottles, and to agitate them occasionally. At the expiration of this time, the bottles were opened, and the alcohol separated and distilled. A semifluid residue was thus obtained, which was filtered at 100° C. It was very dark in colour, owing to the presence of a considerable quantity of a tarry matter, which was ultimately removed by exposing the residue to a powerful freezing mixture, and pressing it, while in the mixture, between folds of bibulous paper, as long as the paper was stained. After this treatment, there remained a crystalline mass, which was almost white. This was finally washed with a small quantity of ether, and dissolved in the same liquid. The residue obtained on evaporating the ethereal solution is the body in question. Dried at 100° C., it gave by analysis, numbers agreeing with the formula $C_4H_4Cy_2$.

This is, I believe, the first example of a diatomic cyanide. It has the following properties :—Below the temperature of 37° C. it is a crystalline solid of a light-brown colour, above that temperature it is a fluid oil. It cannot be distilled. Nevertheless it bears a tolerably high temperature without suffering much decomposition. Its specific gravity at 45° C. is 1·023. It is very soluble in water and alcohol, and sparingly soluble in ether. It has an acrid disagreeable taste. It is neutral to test-paper. Gently warmed

with potassium, it is decomposed, cyanide of potassium being formed in large quantity. Its solution in water is not precipitated by nitrate of silver.

Action of Potash on Cyanide of Ethylene. Formation of Succinic Acid.

An alcoholic solution of crude cyanide of ethylene was prepared in the manner already described, and introduced, together with some sticks of caustic potash, into a large balloon with a reversed Liebig's condenser attached to it. Heat was then applied by means of a water-bath, which caused torrents of ammonia to be evolved. As soon as the evolution of this gas had ceased, the alcohol was distilled off, and in order to secure the complete decomposition of the cyanide, the residue was treated with a solution of potash, and exposed to heat as long as the slightest evolution of ammonia could be detected. A considerable excess of strong nitric acid was then cautiously added, and the whole evaporated to dryness. The nitric acid destroys all the impurities present, and leaves a mixture of nitrate of potash and a free acid, easily separable by means of alcohol, which dissolves the latter but not the former. The acid obtained, on distilling off the alcohol, was twice crystallized from water, dried at 100° C., and analysed. The numbers obtained agreed perfectly with the formula of succinic acid $C_8H_6O_8$.

A silver-salt* was also prepared and analysed. It gave 63·87 p.c. silver, and 14·49 carbon, instead of 65·06 of the former, and 14·46 of the latter, as required by the formula $C_8\ H_4\ Ag_2\ O_8$.

The acid possessed also all the properties of succinic acid. It melted a few degrees above 180° C., and sublimed on the application of a higher temperature. It was very soluble in water and alcohol, and sparingly soluble in ether. It gave when neutralized, a reddish-brown precipitate with sesquichloride of iron. Moreover on digesting this precipitate with amonia, and filtering, an acid could be detected in the filtered liquor, which gave white precipi-

* The acid from which this salt was prepared was obtained in a somewhat different manner. Instead of liberating it from its combination with potash by means of nitric acid, hydrochloric was employed. The whole was then evaporated by a gentle heat, and the residue repeatedly digested with absolute alcohol. On evaporating the alcohol, the succinic acid was obtained free from the chloride of potassium which accompanied it. The silver-salt evidently contained a trace of an acid having a higher atomic weight than succinic acid.

tates with nitrate of silver, and with a mixture of chloride of barium and alcohol. On passing a stream of hydrochloric acid gas through a solution of the acid in absolute alcohol, an oil insoluble in water was obtained, which distilled between 220° and 225° C. This was evidently succinic ether.

The above is an easy and a productive process, and yields the acid at once in a state of purity. From 1,500 grains of bromide of ethylene, I obtained 480 grains of succinic acid, or nearly 33 per cent.

I have studied, in addition, the action of some acids and of nitrate of silver on cyanide of ethylene.

Action of Nitric Acid on Cyanide of Ethylene.

When cyanide of ethylene and nitric acid are evaporated together on a water-bath, a white crystalline mass is obtained. This proved to be a mixture of succinic acid and nitrate of ammonia. The acid can be completely separated from the nitrate by means of ether, of which, however, a large quantity is requisite A silver-salt of the acid was prepared and analysed. It gave 64·07 instead of 65·06 per cent. of silver.

Action of Hydrochloric Acid on Cyanide of Ethylene.

A mixture of cyanide of ethylene and an excess of strong hydrochloric acid was exposed for a few hours in a sealed tube to the temperature of 100° C. On cooling, the contents of the tube became a mass of crystals, which were ascertained to be a mixture of succinic acid and chloride of ammonia. The following equation will explain the reaction:—

$$C_4H_4Cy_2 + 2HCl + 8HO = C_8H_6O_8 + 2NH_4Cl$$

This reaction enabled me to determine the amount of nitrogen in the cyanide of ethylene in a very easy manner. It was simply necessary to perform the above experiment on a weighed quantity of the cyanide, and afterwards to ascertain the amount of nitrogen in the mixed crystals by means of bichloride of platinum in the usual way.

Action of Nitrate of Silver on Cyanide of Ethylene.

About three equivalents of crystallized nitrate of silver were rubbed up in a mortar with one equivalent of pure cyanide of

ethylene and a considerable quantity of ether. The ether was then poured off, and the residual salt dissolved in boiling alcohol. On cooling, the alcohol became a mass of brilliant pearly plates. These were washed with ether, dried at 100° C., and analysed. The numbers obtained led to the formula $C_4H_4Cy_2 + 4\,(AgO.\,NO_5)$.

That this body is simply formed by a union of the cyanide and nitrate in these proportions without decomposition, is confirmed by the fact that, when the crystals are treated with strong hydrochloric acid and the whole evaporated on a water bath, succinic acid can be detected in the residue. The acid is evidently formed by the action of the liberated nitric acid on the cyanide of ethylene. The crystals are soluble in water and alcohol, but insoluble in ether. When heated they explode like gunpowder. They do not, however, detonate on percussion. This compound may possibly throw some light on the constitution of the fulminates. When treated with nitrous acid (NO_3), it gives a remarkable silver-salt, which is insoluble in alcohol, and so fusible, that it can be melted under that liquid.

I have endeavoured to substitute two equivalents of bromine for the two of cyanogen in the cyanide of ethylene, so as to regenerate bromide of ethylene, but without success, the molecule being completely broken up by the action of the bromine.

We are now in a condition to answer the question proposed at the commencement of this paper. Succinic acid *can* be obtained from glycol in the same manner as propionic acid from ordinary alcohol, the bromide of ethylene, the point from which I started being capable of derivation from the diatomic alcohol.

We are now enabled, thanks to the researches of Messrs. Perkin and Duppa, and of M. Kekulé*, to build up three highly complex organic acids (succinic, paratartaric, and malic) from a simple hydrocarbon; and what is more important, we are enabled to do this by processes, every stage of which is perfectly intelligible.

The question now arises: Is the foregoing reaction capable of general application? Can the homologues of succinic acid be obtained in a similar manner? With the view of determining this point, I have endeavoured to prepare pyrotartaric acid from the cyanide of propylene, the radical of propyl-glycol.

* Quarterly Journal of the Chemical Society, July, 1860; and Bulletin de la Société Chimique de Paris, 10 Août, 1860, p. 208.

Preparation of Cyanide of Propylene.

This body, which forms the first step in my process for pyrotartaric acid, I succeeded in obtaining in the following manner:—A mixture of one equivalent of bromide of propylene and two of cyanide of potassium, together with a considerable quantity of alcohol, was exposed to the temperature of a water-bath in well-corked soda-water bottles for about sixteen hours. Their contents were then filtered, and the alcohol distilled off the filtered liquor. A liquid residue was thus obtained, which was very black, and by no means of a promising appearance. This was filtered at 100° C., and digested with ether, which left a large quantity of a black tarry matter undissolved. The residue obtained on evaporating the ethereal solution was then submitted to distillation. Almost all the liquid passed over between 265° and 290° C. The fraction distilling between 277° and 290° gave, by analysis, numbers agreeing approximately with the formula $C_{10}H_6N_2$.

I do not think it possible to obtain this body in a state of purity, unless by fractional distillation *in vacuo*, since it suffers partial decomposition when distilled in air, as evidenced by a slight evolution of ammonia during the process.

The properties of this cyanide very much resemble those of the preceding. It differs however in its physical state, which is that of a liquid at the ordinary temperature of the air. It is soluble in water, alcohol, and ether; has an acrid taste; is colourless and neutral to test-paper. It is decomposed with great facility by potassium, cyanide of potassium being formed in large quantity. Its solution in water gives no precipitate with nitrate of silver. Heated with potash, it forms an acid and gives off ammonia.

Formation of Pyrotartaric Acid.

A mixture of one volume of cyanide of propylene, distilling between 265° and 290° C., and about 1½ volume of strong hydrochloric acid, was exposed in a glass tube hermetically sealed to the temperature of a water-bath for about six hours. Long before the expiration of this time, the contents of the tube had become a mass of crystals. These were dried at 100° C., and dissolved in absolute alcohol. The residue obtained on evaporating the alcoholic solution was then twice crystallized from water, and finally dissolved in ether, in order to remove the last traces of the ammoniacal salt formed in the process. The body

obtained on distilling off the ether is the acid in question. Dried at 100° C. it gave, by analysis, numbers corresponding with the formula of pyrotartaric acid.

It had also all the properties ascribed to this acid by Pelouze and Arppe. The crystals were colourless and very soluble in water, alcohol and ether. It had an agreeable acid taste, and expelled carbonic acid from its combinations with the alkalies. It became semifluid at 100° C., and melted completely a few degrees above that temperature. Long-continued ebullition in a glass tube converted it into an oil, which was insoluble in cold water, and no longer affected litmus paper, but gradually dissolved in boiling water, recovering at the same time its acid reaction. Lime-water was not affected by a solution of this acid. Neutralized by ammonia, it gave a white curdy precipitate with nitrate of silver. Acetate of lead caused no precipitate with the neutralized acid. On the addition, however, of alcohol to the mixed solutions, a bulky white precipitate was obtained, which melted into oily drops on heating the liquid in which it was suspended. The following equation will explain the reaction which gives rise to this acid:—

$$C_6H_6Cy_2 + 2HCl + 8HO = C_{10}H_8O_8 + 2NH_4Cl.$$

Pyrotartaric acid bears the same relation to propyl-glycol that butyric acid bears to propylic alcohol:—

$\underbrace{C_6H_8O_4}$	$\underbrace{C_6H_8O_2}$
Propyl-glycol.	Propylic Alcohol.
$\underbrace{C_{10}H_8O_8}$	$\underbrace{C_8H_8O_4}$
Pyrotartaric Acid.	Butyric Acid.

The claims of this acid to be considered as the homologue of succinic acid, which some chemists do not recognize, are now, I think, fairly established, seeing that these two acids can be obtained by similar processes from homologous hydrocarbons.

The foregoing reaction, which, I think, we may now look upon as capable of general application, will no doubt place in our hands some of the missing acids of the succinic series.

It is highly probable that there exists a series of isomeric acids running parallel to these, which may be obtained by similar processes from the diatomic radicals contained in the aldehydes. Thus from the cyanide of ethylidene ($C_4H_4Cy_2$) we may hope to get an isomer of succinic acid.

The reactions just described lend, I think, some support to Frankland and Kolbe's view of the constitution of these acids, namely, that they are composed of two equivalents of carbonic acid, in which two equivalents of oxygen are replaced by a diatomic radical. However this may be, it is convenient, at all events, to formulate these bodies according to the carbonic acid type :—

$$\underbrace{2HO,\ C_4H''_4\begin{pmatrix}C_2O_2\\C_2O_2\end{pmatrix}O_2}_{\text{Succinic Acid.}} \qquad \underbrace{2HO,\ C_6H_6''\begin{pmatrix}C_2O_2\\C_2O_2\end{pmatrix}O_2}_{\text{Pyrotartaric Acid.}}$$

I propose to continue my researches in this direction, and to extend them to the cyanides of the triatomic radicals.

XXVII.—*On the transformations of Citric, Butyric, and Valerianic Acids, with reference to the artificial production of Succinic Acid.*

By Dr. T. L. Phipson,

[Abstract.]

The author's experiments confirm the result formerly obtained by How and by Dessaignes, that citrate of lime fermented in contact with putrefying casein, yields butyric but not succinic acid. Now as malic acid, which has nearly the same composition as citric acid, has been shown by Dessaignes to yield, under similar circumstances, first succinic and then butyric acid, it appeared not improbable that citric acid might also, by certain modifications of the conditions of the decomposition, be made to yield succinic acid.

Citrate of soda, mixed with a considerable quantity of carbonate was therefore fermented for some weeks with uncooked putrid beef; the products obtained were butyric acid, a compound which imparted a peculiar odour to the liquid, and carbonic acid which converted the carbonate of soda into bicarbonate :

$$\underset{\text{Citric Acid.}}{C_{12}H_8O_{14}} = \underset{\text{Butyric Acid.}}{C_8H_8O_4} + 4CO_2 + O_2$$

but no succinic acid.

Citrate of lime, however, fermented with a small quantity of boiled beef, yielded butyric acid and a small quantity of succinic acid.

Citric acid oxidised by permangate of potash at a temperature a little above summer-heat, was found to yield nothing but oxalic acid:

$$\underset{\text{Citric Acid.}}{C_{12}H_8O_{14}} + O_{12} = 3\underset{\text{Oxalic Acid.}}{C_4H_2O_8} + 2HO.$$

Butyrate of lime oxidised by permanganate of potash at a temperature a little below the boiling point of the liquid, yielded succinic acid and acetic acid:

$$2C_8H_8O_4 + O_{10} = C_8H_6O_8 + 2C_4H_4O_4 + 2HO.$$

The acetic acid unites with the butyric acid to form butyro-acetic acid, a compound which obstinately resists the ordinary action of the permanganate. Nevertheless, the conversion of butyric acid into succinic acid in this manner, was found to be much more rapid than by oxidation with nitric acid, the process formerly pointed out by Dessaignes.

Valerianic acid treated with permanganate of potash yields, in like manner, succinic acid and aceto-valerianic acid.

The ethyl-compounds of butyric and valerianic acids are oxidised by the permanganate more quickly than the acids themselves.

The author considers it probable also that suberic acid may be formed in small quantity in these reactions.

XXVIII.—*On a mode of taking the Vapour-density of Volatile Liquids at temperatures below the boiling point.*

By Dr. Lyon Playfair, C.B., F.R.S., and J. A. Wanklyn, F.R.S.E.

[Abstracted from the transactions of the Royal Society of Edinburgh, Vol. XXII., Part III.]*

It is commonly said that vapour-densities taken at high temperatures are more correct than those taken at low temperatures.

* This abstract has been revised by the Authors, who have added some additional matter.

A more accurate statement of the case is—vapour-densities taken at a distance from the point of liquefaction are more correct than those taken near that point.

When a vapour approaches the point at which it passes into the liquid state, it loses some of the characteristics of a true gas, it ceases to expand quite uniformly for equal increments of heat, and it manifests a tendency to condense on the sides of the containing vessel. Either of these properties would make the determination of a vapour-density abnormal.

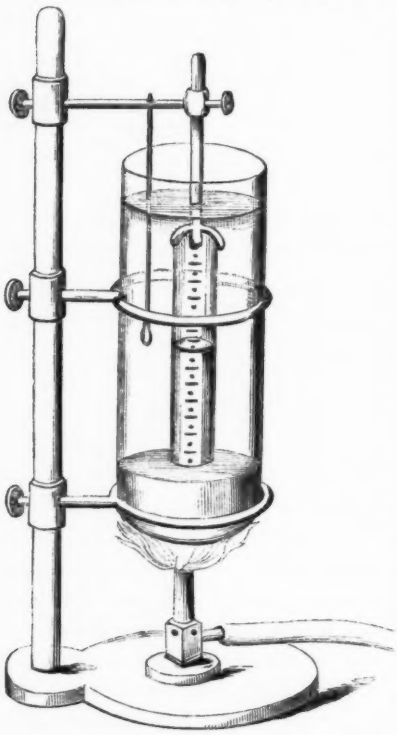
We are, however, inclined to believe that the effects upon the density, which are really due to these causes, have been exaggerated. The examples about to be brought forward show that only a moderate distance (measured either in temperature or in pressure) from the point of liquefaction is enough to render the density of a vapour nearly normal.

We believe that, in the few cases where any great difference is found between a vapour-density taken at a point moderately removed from the point of liquefaction, and one taken at a point far removed from the point of liquefaction, there is a chemical and not a merely physical change. Thus we hold that sulphur-vapour has sometimes one and sometimes another chemical formula, according as it is more or less heated. Peroxide of nitrogen, which we shall show has two radically distinct densities at high and low temperatures, has the composition N_2O_8, at ordinary temperatures and NO_4 at the temperature of boiling water.

A vapour may be removed from its point of liquefaction, either by raising its temperature, or by diminishing the pressure upon it, or by adding a certain quantity of a permanent gas to dilute it. If it be required to take a vapour-density at a low temperature, the vapour must be removed from its point of liquefaction by one or other of the latter methods. We propose to introduce the employment of the last-named method, to mix vapours with permanent gases instead of lowering the barometric pressure. We shall point out as we proceed, the practical advantages which the method of dilution has over the method of directly diminishing the barometric pressure. Here we bring forward experiments to prove that such dilution is really effective in rendering the density of vapours normal.

For this part of the enquiry, a slight modification of Gay Lussac's method of determining vapour-densities was found to be most convenient. A carefully dried graduated tube is

filled with warm mercury, and inverted in the mercurial trough. Next, dry hydrogen is introduced. The gas is then measured, adopting the precautions which are requisite in measurements for a gas analysis. The liquid to be operated upon, of which a weighed portion is contained in a small glass bulb, is subsequently passed up to the hydrogen contained in the graduated tube. The tube, with its contents, is then lifted out of the mercurial trough by means of a small iron cup, and transferred to the bath in which it is to be heated, and which contains some mercury, occupying about an inch of its interior. An adjustment of the graduated tube having been made, water is poured into the bath, and heat applied, until the boiling-point of the liquid under examination has been passed. After all the liquid contained in the bulb has evaporated, the bath is allowed to cool very slowly, being stirred up constantly, so as to keep its temperature uniform throughout. Before each observation, great care was taken to ensure uniformity of temperature.



The following minute corrections were made:—

1. A correction for meniscus equal 0·3 cubic centimeter.

2. A correction for expansion of the glass tube, which amounts to from ·40 cubic centimeter to 0·1 cubic centimeter.

Both the barometric column and the mercurial column contained in the graduated tube were reduced to zero, according to tables given for that purpose in Bunsen's "Gasometry." The water column occupying the bath was measured in millimeters, corrected for temperature, and reduced to mercurial measure.

Series of Experiments with Slightly Moist Alcohol.

	Observed volume in Cub. Centimeters.	Temperature C.	Pressure in Millimeters.	Vol. in Cub. Cent. corrected at 0° C. and 760 m.m. Pressure.
Dry Hydrogen	68·18	7° C.	600	52·482
Dry Hydrogen and Alcohol Vapour—Observation 1,	130·94	101°	732·9	92·189
Dry Hydrogen and Alcohol Vapour—Obs. 2, ..	126·04	84°	724·6	91·916
Dry Hydrogen and Alcohol Vapour—Obs. 3, ..	124·28	77·5°	720·9	91·840
Dry Hydrogen and Alcohol Vapour—Obs. 4, ..	122·68	70·5	717·9	92·117
Dry Hydrogen and Alcohol Vapour—Obs. 5, ..	120·02	61°	712	91·922

The numbers contained in the last column are obtained from those in the other columns, by applying Marriotte's law, and using the coefficient ·00366 for the expansion of 1° C. Inspection will show that the pressures are nearly alike in the five observations made of hydrogen mixed with alcohol-vapour, whilst the temperatures vary 40° C.

Since the numbers in the last column are almost identical, it follows that the coefficient of expansion adopted in their calculation is correct.

The alcohol in this instance was supposed to have been dry, but subsequent examination showed that a small quantity of water had escaped the action of the dehydrating agents. The vapour-density of this moist alcohol may be found by the following calculation. We will take Observation 1 :—

	Cubic cent.
Vol. of hydrogen + alcohol vapour	= 92·189
Vol. of hydrogen	= 52·482
	39·707

The weight of the alcohol which was introduced was ·0775 grm.
Therefore, 39·707 cub. cent. of alcohol vapour weigh ·0775 grm.
39·707 cubic cent. of air weigh ·05137 grm.

$$\frac{\cdot 0775}{\cdot 05137} = 1\cdot 508,$$ the vapour-density of the moist alcohol.

If the other observations be calculated, the numbers will be found to differ very little from that obtained from the first; indeed Observation 3rd, which departs furthest from Observation 1st, gives for the vapour-density the quantity 1·522.

The same sample of moist alcohol was made the subject of an experiment, in which its vapour-density was determined in the usual way, without the employment of a permanent gas :—

The results were :—

Temperature.	Vapour-density.
95°	1·551
83°	1·565

In the first described experiment, where hydrogen was present, we found the vapour-density of the alcohol to lie between 1·508 and 1·522. It would appear, therefore, that the presence of hydrogen lowers the density of alcohol vapour; the lowering cannot be due to difference of pressure; for in the experiment where the higher vapour-density was obtained, the pressure was about 630 millimeters, whilst in the other experiment it was about 730.

Experiments on perfectly Anhydrous Alcohol.

Weight of the Alcohol taken = ·0889. grm.

	Observed volume in Cub Centimeters.	Temperature C.	Pressure in Millimeters.	Vol. in Cubic Cent. corrected at 0° C. and 760 Millimeters.
Vol. of Dry Hydrogen ..	43·16	7°	572·07	31·676
Hydrogen and Alcohol Vapour—Observation 1, ..	110·84	99°	710·6	76·073
Hydrogen and Alcohol Vapour—Obs. 2, ...	107·16	83·5°	699·7	75·565
Hydrogen and Alcohol Vapour—Obs. 3, ...	102·74	68°	695·1	75·238

A correction of 0·4 cub. cent. for air contained in the alcohol bulb has to be made. This quantity must be subtracted from the volume of alcohol vapour.

The vapour-densities, as deduced from the three observations, are as follows:—

	Vapour-Density.
Observation 1 at 99° . .	1·562
„ 2 at 83·5° . .	1·580
„ 3 at 68° . .	1.592

The same sample of anhydrous alcohol gave without hydrogen:—

Temperature.	Vapour-density.
At 100·5° . .	1·599
At 86·5° . .	1·602

Here, again, we notice the same peculiarity as in the former experiments with the specimens of moist alcohol, viz., the vapour-densities taken with hydrogen are rather lower than those taken without it.

The theoretical vapour-density of alcohol calculated from the specific gravity of hydrogen is $\frac{46}{2} \times 0691 = 1·5893$, a number which agrees with our experiment.

In several elementary works on Organic Chemistry, in Regnault's "Manual" for example, the following vapour-densities for alcohol at different temperatures are given:—

Temperature.	Vapour-density.
88° C.	1·725
98°	1 649
110°	1·610
125°	1·603
150°	1·604
175°	1·607
200°	1·602

Our observation does not confirm the decrease of ·08 in density between 88° C. and 98° C. Between 86·5° and 100·5°, we have an decrease of ·003 only.

Experiments made in like manner with Ether which had been purified and dried with great care, gave:—

With hydrogen:—

	Temperature.	Vapour-density.
At .	69·5° C. . .	2·499
At .	20·8° . .	2·539

Without hydrogen:—

	Temperature.	Vapour-density.
At	94° C.	2·541
At	52° C.	2·580

The theoretical vapour-density of ether is $\frac{74}{2} \times 0691 = 2{\cdot}5567$.

These experiments show that admixture of hydrogen with the vapour of alcohol or ether renders it capable of being cooled down much below the boiling point, without losing its normal density.

Some experiments by Regnault, undertaken for meteorological purposes, have shown that the aqueous vapour suspended in the atmosphere has the normal-density 0·622. We may, therefore, regard the first question as satisfactorily answered.

But whether it is *more* effective to add a permanent gas than to diminish barometric pressure, will require a set of very careful experiments. The practical advantage of using the gas, rather than lowering the pressure, will be evident from the following considerations:

Let it be required to expand 10 cub. centimeters of a vapour to double the volume. To do so, half the barometric pressure must be taken off by means of a column of mercury between the lower level of the gas and the level of the mercury in the trough.

We thus get volume = 20 C.C.; mercurial column in the bath = $\frac{1}{2}$ barometric height.

But let the expansion be made by adding an equal volume of permanent gas, and we have volume of gas and vapour = 20 C. C.; mercurial column in the bath = 0.

Thus it appears that by using a gas the long mercurial column is saved. Several other advantages attend the use of the gas; but the circumstance that the gas requires an apparatus only of the ordinary size, while to work at low pressures would require at least double the ordinary capacity of tube, bath, and everything else, is alone sufficient to make the former method much more practicable than the latter.

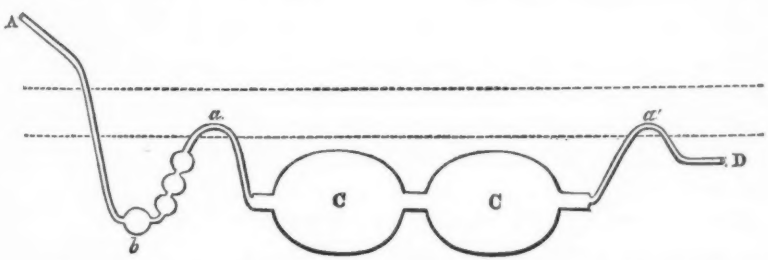
We next describe the way of proceeding when it is desirable to avoid heating the substance which is operated upon, when a degree of heat approaching that at which the substance boils would produce decomposition.

By the plan about to be described, the vapour is never heated higher than the temperature at which its density is to be taken.

The principle is that of Dumas' method—viz., the weighing of a given volume of vapour: the mode of carrying it out is, however, so different, that a minute description of the apparatus will be necessary.

Those who have occupied themselves with Dumas' mode of taking vapour-densities, will be well aware, that one of the difficulties of using it for temperatures near the boiling point of a liquid, is due to the circumstance that it is impossible to know when all the liquid has assumed the state of vapour.

Our modification of the method consists in placing the liquid to be vaporized outside of that part of the apparatus which, when hermetically sealed, will contain the vapour mixed with gas. The apparatus consists of a pair of large bulbs, connected together by means of a neck, and terminating on either side in narrow glass tubes, which are bent and blown into small bulbs, as represented in the drawing. The bulbs C and C are large, and together capable of holding from 200 to 400 cubic centimetres. The bulbs *b* are very small, being mere dilations of the narrow tube. They are to contain the liquid to be examined. The bends *a* and *a* should be



on the same level, and thin, so as to admit of fusion by the lamp. Altogether the apparatus should not weigh more than 65 grm. The following mode is employed in making an experiment with the apparatus.

After being cleaned and filled with the dry air of the balance-case, the bulb-apparatus is weighed, and then transferred to the bath, being grasped by a retort-holder, which takes hold of the neck connecting the large bulbs C and C. The end A is then jointed to a hydrogen-apparatus by means of a small caoutchouc tube; the other extremity D, which projects out of the bath through an orifice in the side of that vessel, is likewise connected, by means of a caoutchouc tube, with a long narrow glass tube pointing downwards, and designed to prevent diffusion. Dry

hydrogen gas is then passed through the apparatus to repletion. Whilst this is going on, warm water is poured into the bath—the hole in its side through which the extremity D passes being stopped up with putty, which makes a very convenient water-tight stopping. The addition of water is continued, until the bends *a a* are totally submerged. When the apparatus is full of hydrogen, the connection at A is interrupted, and the liquid, of which a vapour-density determination is made, introduced at A.

On re-establishing the communication with the hydrogen-apparatus, a stream of dry hydrogen passes through the dilatation *b*, and becoming more or less saturated with vapour, enters the great bulbs C and C.

No more liquid is placed in *b* than is sufficient to fill that bulb half-full, the three suplementary dilatations near *b* acting as safety-bulbs, to avoid the effects of splashing.

The temperature of the bath is raised very slowly, the water being constantly stirred, so as to ensure uniformity of temperature When the temperature is three or four degrees below the point at which a vapour-density determination is required, the current of hydrogen is nearly stopped.

The object of this is to avoid complete saturation of the gas with vapour. By this device, the greater part of the gas which is present in C and C, at the end of the operation, has entered at a lower temperature than that at which the apparatus is sealed, and, consequently, is only partially saturated at the moment of sealing the apparatus.

The desired temperature having been attained, sufficient water to expose the bends *a a*, but not the large bulbs C C, is suddenly let out of the bath, by opening a large tap situated close to the bottom of the bath. The current of hydrogen having been entirely stopped, the flame is applied to *a* and *a*, until the apparatus is sealed up in both places. The temperature of the bath having been again noted, and also the height of the barometer, the bulbs C and C which contain the vapour and hydrogen, are removed from the bath, carefully cleaned, and subsequently, along with the other two fragments (viz., the portion A to *a* and the portion *a* to D, also carefully cleaned), transferred to the balance-case and weighed.

The difference between this latter weighing and that at the beginning of the operation gives, when the weight of the displaced air is added to it, the weight of C C filled with a mixture of

hydrogen and vapour at the barometric pressure and temperature of the bath at the time of sealing.

The remainder of the operation having for its object to find how much hydrogen is enclosed in C C, and also the capacity of C C, is conducted thus:—The hermetically sealed C C, is placed in cold water, and one of its sealed extremities nipped off whilst still under water, which enters and occupies the space not filled with hydrogen. After remaining in water for a number of hours, until the vapour has been completely absorbed, the apparatus is lifted vertically out of the water, care being taken not to heat the hydrogen contained in the bulbs, for which purpose a holder is employed. The temperature of the water is observed; also the height of the barometer.

The apparatus, together with the water which has thus entered, is then weighed. It is afterwards completely filled with water, and again weighed.

The difference between the weight of the bulbs empty, and filled with water, gives the total capacity of the apparatus.

The difference between the weight after the first portion of water has entered, and the weight of the apparatus quite full of water, gives the volume of the hydrogen at the temperature of the water and at the barometric pressure, minus the column of water contained in the bulbs when they are held over the water out of which they had been lifted. This column is measured after the first weighing of bulbs and water has been made.

Such is the process which we employ to take vapour-densities of bodies incapable of being heated to their boiling points without decomposition.

Exception may perhaps be taken to the mode of measuring the hydrogen included on sealing the bulbs. We will answer some objections which might naturally be raised.

It might be feared that the vapour would not be perfectly absorbed by water; but when it is considered how much water there is, and how little vapour has to be acted upon by it, it will be evident that only in those instances where the vapour is nearly insoluble in water, will there be any chance of appreciably incomplete absorption. Only in those instances where the substance is at once insoluble in water and possesses a high tension at ordinary temperatures, could error arising from this source become serious.

With regard to the absorption of hydrogen by water, it may be

remarked that since between 8° and 11° C, the absorption-coefficents of hydrogen and common air, as determined by Bunsen, are nearly identical, the measurement of hydrogen over water is so far unobjectionable.

As an example of the method, we subjoin the particulars of a vapour-density determination of absolute alcohol, made 30° C. below its boiling point:—

Barometer (corrected to 0° C.) = 763·094 m.m.
Temperature of the balance-case, 7·5° C.
Weight of apparatus in dry air, = 69·959 grm.
Temperature at the time of sealing 48° C.
Weight of the apparatus + H + vapour = 69·5275.
Weight of apparatus + water (at 5·2° C.) = 191.76 grm.
water column, 122 m.m.
Weight of apparatus filled with water = 545·36 grm.

	Volumes corrected at 0° C, and 760 m. m. pressure, Cubic centimetres.		grm.
Hydrogen + vapour,	406·43	weighing	0·1695
Hydrogen,	341·27	,,	0·0306
	65·16		0·1389

Therefore, 65·16 cub. c. of alcohol vapour weigh ·1389 grm.
But 65·16 cub. c. of air weigh ·0843 grm.

$$\text{Vapour-density of alcohol} = \frac{\cdot 1389}{\cdot 0843} = 1\cdot 648.$$

Two experiments made upon very small quantities of water showed results almost as near the theoretical quantity as the balance will admit. In neither case did the weight of aqueous vapour each 10 milligrammes:—

Exp. 1. Vapour-density of water = 0·671.
Exp. 2. Vapour-density of water = 0·654.

$$\text{Theoretical density of water, } \frac{18}{2} \times 0\cdot 691 = 0.6219.$$

When Dumas' method of vapour-density determination is employed, the practical advantages of diluting with a gas rather than working at diminished pressures are very obvious. We may call attention to two points.

When the gas is used, in the manner described above, the sealing up of the apparatus is managed whilst there is no difference between the pressure inside and outside. Let the apparatus be connected with an air-pump, and let the attempt be made to work in vacuo, and great difficulty will be experienced in quickly sealing up at the bends of the apparatus.

Further a very thin and light glass vessel may be used when gas is employed; for when the sealed bulbs become cold, they have to withstand only a fraction of the barometric pressure; and, precisely in those cases where the lightest and largest bulbs are desirable, where the proportion of vapour to gas is the smallest, just there does it happen that the fraction of barometric pressure to be afterwards withstood is the very smallest.

Experiments upon Acetic Acid vapour.

Cahours has obtained by the usual processes;

	Temperature.	Density.
Density of acetic acid vapour at	125° C .	3·180
„	„ 150 .	2·727
„	„ 200 .	2·248
„	„ 270 .	2·098

		Vapour-density.
The theory requires	$C_4H_4O_4$.	2·073
	$C_8H_8O_8$.	4·146

Stated in general terms, our results are:—by adding hydrogen, a vapour-density of 2·073 can be got at least as low as 150° C.; whereas at 60° C., even in spite of 16 vols. of hydrogen to one of vapour, the vapour-density of acetic acid approaches to 4·0

Instances of the employment of the foregoing methods.

Nitrate of Ethyl.—Among the nitrates, the nitrate of methyl alone has been made the subject of a vapour-density determination. Bodies of this kind become explosive on being raised only a few degrees above their boiling points, and hence are difficult to treat by the usual methods.

We have deemed it interesting to estimate the vapour-density of nitrate of ethyl.

The vapour-density determination was made by the modification of Gay-Lussac's method. The gas employed as the diluent was dry nitrogen.

The results were—

Temperature.	Vapour Densities.
at 85·5°C	3·112
„ 90°	3·094
„ 70·3°	3·065
„ 64·9°	3·079

$\left.\begin{matrix}C_4H_5\\NO_4\end{matrix}\right\}O_2$ requires $\frac{91}{2} \times \cdot 0691 = 3 \cdot 144$, which is sufficiently near the experimental density.

Nitric Acid.—It can hardly be said that the state of condensation of the acids has been determined by direct experiment. Most of the acids are too little volatile, or suffer decomposition at temperatures too low to admit of such experiments. And those acids whose vapour-densities have been actually observed are seldom in perfect accordance with theory. The vapour-density of sulphuric acid, for example, is abnormal: and although we are far from demurring to the explanation that that acid suffers decomposition into anhydride and water, it must be allowed that direct experiment has not yet established the molecular weight indicated by the formula $\left.\begin{matrix}S_2O_4\\H_2\end{matrix}\right\}O_4$

Again, the series of fatty acids, although normal at high temperatures, are abnormal at low temperatures: indeed, it is difficult to find an example of an acid which does not offer some anomaly of the kind.

We have selected nitric acid for experiment. As will be apparent by-and-by, this acid is regular, having for its molecular weight the number answering to the formula $\left.\begin{matrix}NO_4\\H\end{matrix}\right\}O_2$

The acid employed was distilled from sulphuric acid, then from dried sulphate of copper, and lastly, warmed in a stream of dry carbonic acid, so long as its colour became less yellow. The final product was found to be quite free from sulphates and chlorides. Its strength, as indicated by alkalimetry, was satisfactory. Its colour was a very pale yellow, which the transmission of carbonic acid was incapable of rendering fainter.

From our observation, we are inclined to believe that the last yellow tinge cannot be removed from monohydrated nitric acid by

warming for any length of time in a current of perfectly dry gas; but the presence of a minute trace of moisture in the transmitted gas at once decolorises the acid. The success of the employment of urea as a means of depriving nitric acid of colour, depends partly on the production of water. We need hardly remark that we avoided the use of urea. We believe, moreover, that the quantity of peroxide of nitrogen requisite to give the yellow tinge is imponderable.

As nitric acid attacks mercury, Gay-Lussac's process is quite innapplicable to it; and since nitric acid undergoes some decomposition on boiling, Dumas' process would not answer without some modification.

The following determinations have been made by the method previously described. The gas used to dilute the nitric acid vapour was dried air.

I.

Determination of Vapour-density of Nitric Acid at 68·5° *C.*

	Cubic Centimeters at 0° C. and 760 m. m.		Grm.
Vol. of Air + Vapour =	384·60	weighing	·7255
„ Air =	962·48	„	·3395
	132·12		·3860

Hence 132·12 cub. cent. of nitric acid vapour weigh ·3860 grm. Vapour density = 2·258. In the above experiment the bulbs, when sealed up, were perfectly colourless.

II.

Determination of Vapour-density of Nitric Acid at 40·5° *C.*

	Cubic Centimeters at 0° C. and 760 m. m.		Grm.
Vol. of Air + Vapour	317·62	weighing	·4664
„ Air	286·28	„	·0705
	31·24		·0959

Hence 31·24 C. C. of nitric acid vapour weigh ·0959 grm. Vapour density = 2.373. In this instance the bulbs were very faintly tinged with peroxide of nitrogen. Possibly this may be the real reason why in this case the number is a little higher than in the former experiment.

The results are :—

Temperature.	Vapour-densities
at 68·5° . . .	2·258
„ 40·5 . . .	2·373

The formula $\left.\begin{matrix}NO_4\\H\end{matrix}\right\}O_2$ requires $\frac{63}{2} \times \cdot 0691 = 2 \cdot 1766$.

It thus appears that nitric acid vapour is nearly normal, even at many degrees below the boiling point, under ordinary atmospheric pressures.

Here the remark may be made, that one of the sources of uncertainty belonging to Dumas' method is avoided. Several grammes of substances are generally taken for Dumas' vapour-density determination. Fractional distillation takes place in course of the operation, so that unless the substance be of extreme purity, the specific gravity obtained is liable to depart widely from the mean specific gravity of the sample.

The method which we have described completely avoids this. Only a small quantity of substance is necessary, and even that need not be completely evaporated, since the portion of the apparatus containing the substance is afterwards separated from the portion filled with gas and the vapour.

Peroxide of Nitrogen NO_4.—Peroxide of nitrogen offers one of the examples of physical and chemical properties in opposition. Whereas NO_4 represents Cl. (one equivalent of NO_4, replacing just as much as one equivalent of Cl), NO_4 is physically equivalent to Cl_2. The wonderful deepening in colour which peroxide of nitrogen undergoes on being heated, led us to suspect that molecular change might also occur. This expectation has been fully realised. We deduce from our experiments that peroxide of nitrogen exists in two states; that there are two bodies having the same percentage composition as peroxide of nitrogen, but which are polymeric.

The body existing at high temperatures requires the formula NO_4, that existing at low temperatures requires the formula N_2O_8.

The peroxide of nitrogen used in this research was prepared partly by distilling nitrate of lead, and partly by distilling a mixture of nitrate of lead with chloro-chromate of potash. The products from several operations were purified together, and placed in a single hermetically sealed tube. Analysis showed that it was pure.

Before proceeding to take the specific gravity of peroxide of nitrogen at different temperatures by the methods under consideration, it was requisite to settle certain points relating to the reactions of the body.

In a preliminary determination of specific gravity, made by Dumas' method, some months before the chief investigation, it was found that peroxide of nitrogen was completely absorbed by water, without any evolution of NO_2, at any rate at ordinary temperatures. In that experiment, the Dumas flask filled completely with water when opened under water at the end of the determination; and after several days even, no appreciable amount of gas had made its appearance in the flask.

At first we employed air as the diluent gas in these vapour-density determinations, but were subsequently compelled to have recourse to nitrogen: for direct experiment showed that, when a measured volume of air is sealed up with water and peroxide of nitrogen, absorption of oxygen takes place, the ultimate volume measuring much less than the initial volume of air. Notwithstanding this source of error, which would tend to make the peroxide of nitrogen seem lighter than it really was, the specific gravity of that body at 8·5° C. was obtained as high as 2·46.

The following determinations of the vapour-density of peroxide of nitrogen were made, using as the diluent nitrogen gas, prepared by burning phosphorus in air collected in a gas-holder, finally passing through a strong solution of pyrogallate of potash, and dried with sulphuric acid:—

I.

Vapour-density determination at 97·5° *C.*

	Cubic Cent. at 0° C. and 760 m. m.		Grm.
Vol. of $N+NO_4$	263·97	weighing	·4473
„ N .	159·47	„	·2063
	104·50		·2410

Therefore 104·50 c. c. of NO_4 weigh ·2410 grm. Vapour-density = 1·783. Dilute solution of potash (sp. gr. 1·0043) was used to absorb the peroxide of nitrogen. The residual nitrogen was then calculated as being quite saturated with moisture: for potash of so low a specific gravity would not sensibly differ from pure water in point of tension.

In this and the following experiments, it was carefully ascertained that the residual nitrogen was quite colourless: also, on making repeated experiments, no coloration could ever be seen on admitting air to the residual gas.

II.

Vapour-density determination at 24·5° *C.*

	Cubic Cent. at 0° C. and 760 m. m.		Grm.
Vol. of $N+NO_4$	425·29	weighing	·8963
„ N .	244·39	„	·3070
	180·90		·5893

Therefore 180·90 C. C. of NO_4 weigh ·5893 grm. Vapour-density = 2·52.

The absorption of NO_4 was made by means of water.

III.

Vapour-density determination at 11·3° *C.*

	Cubic Cent. at 0° C. and 760 m. m.		Grm.
Vol. of $N+NO_4$	442·05	weighing	·7556
„ N .	349·4	„	·4390
	92·65		·3166

Therefore 92·65 cub. cent. of NO_4 weigh ·3166 grm. Vapour-density = 2·645. In this determination, strong caustic soda (sp. gr. 1·348) was used to absorb the NO_4. In making the calculation, the gas in contact with such a solution was considered half dry. By this means, absolute precision is sacrificed to certainty. It cannot be doubted that the strong alkali would completely absorb all NO_4 without evolving NO_2.

The influence of the possible tension of aqueous vapour from strong solution of caustic soda does not seriously affect the calculation. If we reckon the gas absolutely dry, we get vapour-density of NO_4 = 2·69.

If absolutely wet, we have vapour-density of NO_4 = 2·60.

IV.

Vapour-density at 4·2° C.

	Cubic Cent. at 0° C. and 760 m. m.		Grm.
Vol. of $N+NO_4$	354·38	weighing	·5711
„ N .	294·15	„	·3695
	60·23		·2016

Therefore 60·23 C. C. of NO_4 weigh ·2016 grm. Vapour-density = 2·588.

Here weak solution of caustic potash (sp. gr. = 1.0045) was employed, and considered to have the same tension as pure water.

The results obtained were as follows:—

Temperature.	Vapour-densities.
At 97·5° C	1·783
„ 24·5°	2·520
„ 11·3°	2·645
„ 4·2°	2·588

The vapour-density of NO_4, given in Regnault's "Cours Elémentaire de Chimie;" is 1·72,—a number which is a little less than the first number in the preceding list:—

The formula NO_4 requires $\frac{46}{2} \times ·0691 = 1·5893$.

The formula N_2O_8 requires $\frac{92}{2} \times ·0691 = 3·1786$.

It will be observed that, even at 97·5° C., the vapour-density of peroxide of nitrogen is rather too high for the first formula, whilst at 24·5° and downwards, the vapour density is much nearer that required by the second formula than that required by the first.

If it be allowed that there exist two peroxides of nitrogen, NO_4 and N_2O_8, and that these bodies pass readily into one another, the above results find a simple and natural explanation. At 100° C., the gas consists chiefly of NO_4; at ordinary temperatures, chiefly of N_2O_8; whilst at intermediate temperatures, intermediate quantities of NO_4 and N_2O_8 are present.

If change of composition be denied, the peroxide of nitrogen must have an expansion-coefficient widely differing from that of other gases. To admit such an exception to one of the best physical generalisations, seems unphilosophical.

In general, gases when exposed to pressures not exceeding the usual barometric pressure, and when no incipient liquefaction is

taking place, have an expansion-coefficient not differing widely from ·00366. No exception has yet been established; for, in those cases of which sulphur is the representative, it is at least probable that truly polymeric bodies exist.

Another illustration of the vapour-density methods above described consists in an inquiry into the existence of hydrated oxide of ammonium.

Can hydrated oxide of ammonium exist at 100° C., and in the gaseous state? To solve the problem, a quantity of dry ammonia was measured over mercury, then a small portion of water, which had been accurately weighed in a thin glass bulb, was introduced into the ammonia. The whole was then heated up to 100° C., and the volume of mixed gas and aqueous vapour noted. It will be obvious that the formation of hydrated oxide of ammonium would be indicated by contraction. If, on the other hand, the NH_3 and aqueous vapour, when mixed, had the same volume as when separate, no hydrated oxide of ammonium had been produced.

The following are the details of the experiment:—

	Observed volume in Cub. Centimeters.	Temperature Centigrade.	Pressure in Millimeters.	Corrected Vol. in Cubic Cent. at 0° C. and 760 m. m.
Vol. of dry NH_3, ...	34·19	12·5°	558·08	24·008
Vol. of NH_3 + water, ..	107·32	102°C.	709·66	72.973

·0402 grm. of water taken.

But ·0402 grm. of water, when converted into vapour, measures 49·95 cub. centimeters at 0° C. and 760 mm. The difference between the readings before and after the addition of that amount of water is 48·965 cub. cent. Therefore, at 100° C., ammonia and aqueous vapour can exist side by side without suffering any considerable contraction.